

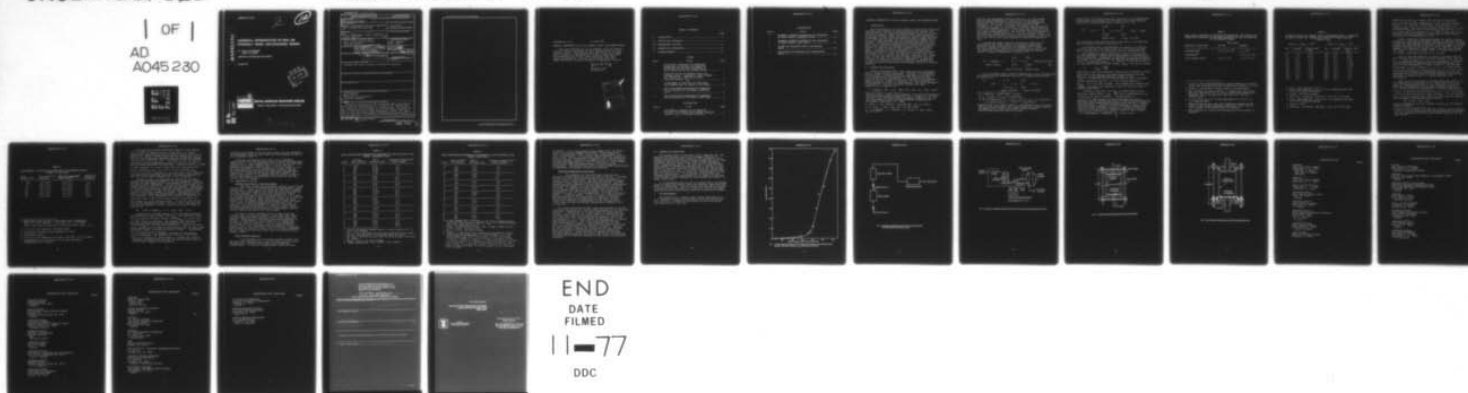
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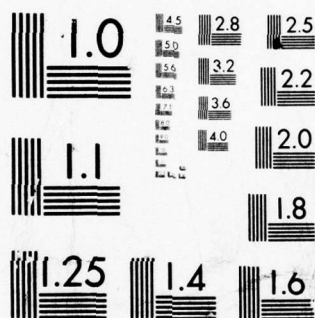
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CHEMICAL DEGRADATION OF RDX ON STRONGLY BASIC ION-EXCHANGE RESINS

BY JOHN C. HOFFSOMMER
DONALD A. KUBOSE

RESEARCH & TECHNOLOGY DEPARTMENT

14 JUNE 1977



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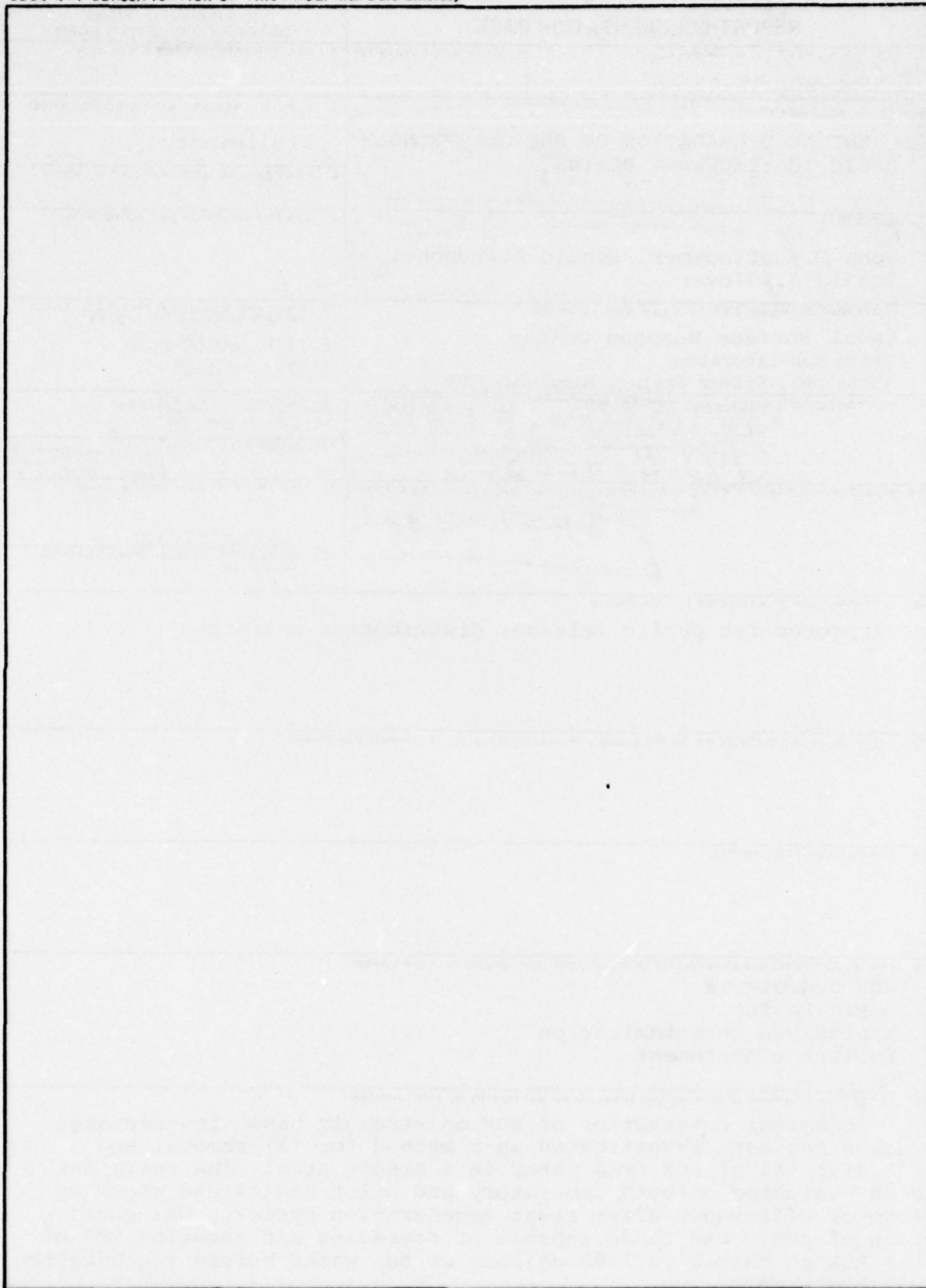
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CHEMICAL DEGRADATION OF RDX ON STRONGLY BASIC ION-EXCHANGE RESINS

This work describes the use of strongly basic ion-exchange resins to remove and dispose of small amounts of RDX in large volumes of water. This approach is a new concept in the waste water treatment of explosives and provides a potential method for decontamination of waste water containing other base sensitive explosives. The work was performed under Task Number SF57572301, Pollution Potential of Explosives in Water.

Julius W. Enig

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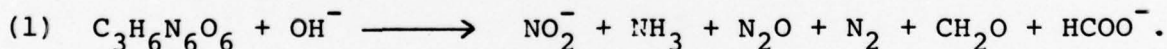
CHEMICAL DEGRADATION OF RDX ON STRONGLY BASIC ION-EXCHANGE RESINS

I. INTRODUCTION

The decontamination of large volumes of waste water containing relatively small amounts of dissolved explosives presents real problems both to the explosives manufacturers as well as to those facilities engaged in demil and Load and Pack (LAP) operations. In the past the most widely used method to remove these explosives contaminants has been physical adsorption which included the use of (1) activated charcoal, and (2) non-functional polymer resin systems¹. Although these adsorptive methods have proven fairly successful in removing certain explosive contaminants from waste water, there remains the problem of regeneration of the spent charcoal or resin and the ultimate disposal of this explosive waste. It seemed worthwhile, therefore, to investigate the chemical interaction of the explosive with a suitable substrate which would both (1) remove the explosive from the water, and (2) dispose of the explosive by chemical interaction in a single step. At the same time, it would be highly desirable that this substrate be easily and efficiently regenerable. We wish now to report our findings concerning an RDX water decontamination process utilizing strongly basic ion-exchange resins as a reactive substrate.

II. RESULTS AND DISCUSSION

Previous investigations^{2,3} have shown that RDX is degraded under a variety of basic conditions. Recently, this degradation has been shown⁴ by deuterium labeling experiments to proceed via a rate determining proton abstraction step followed by rapid ring cleavage of the intermediate, 1,3,5-triaza-3,5-dinitrocyclohexene-1, to yield a number of products, the relative amounts of which depended on the OH⁻ ion concentration. The basic degradation of RDX with OH⁻ ion and the products obtained are shown schematically in reaction (1).



¹Technical Report: "Waste Water Treatment in the Military Explosives and Propellants Production Industry," Vol 3, Chapter 6, Oct 1975, prepared by The American Defense Preparedness Association for the U.S. Environmental Protection Agency Office of Research and Development, Washington, D.C. 20410.

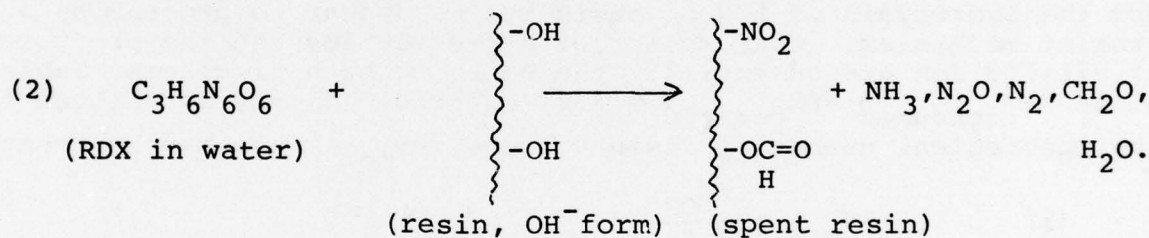
²F. Somlo, Z. ges. Schiess-u. Sprengstoffw., 35, 175 (1940).

³W. H. Jones, J. Amer. Chem. Soc., 76, 829 (1954).

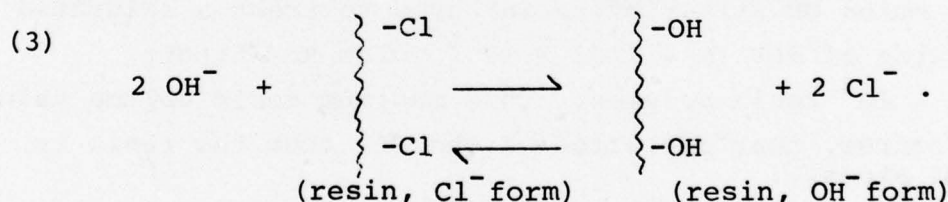
⁴J. C. Hoffsommer, D. A. Kubose, D. J. Glover, J. Phys. Chem., 81, 380 (1977).

From the rate expression⁵ and the value of k_2 , it can be shown that the basic degradation of RDX in water by the addition of sodium hydroxide or lime is not practical as a decontamination procedure. For example, since the time required for 99% degradation is $t_{\text{sec}} = 1.2 \times 10^4 / \text{OH}^-$, 20 minutes would be required to reduce 45 ppm⁶ RDX to 0.45 ppm RDX with an OH^- concentration of 9.8 M (~30% sodium hydroxide). On the other hand since the pH of lime water is approximately 12 ($\text{OH}^- \approx 10^{-2}$ M) the time required for 99% hydrolysis of RDX would be 1.2×10^6 sec or about 14 days. In the first case the amount of sodium hydroxide required is excessive and in the latter case liming requires an impractical amount of time.

A relatively simple method to increase the effective OH^- concentration was found, consisting of passing aqueous RDX solutions through strongly basic ion-exchange resin columns. With this procedure, the RDX was (a) adsorbed by the resin, and (b) chemically interacted with quarternary ammonium hydroxide groups⁶, as shown schematically in reaction (2).



The ion-exchange resin, which as supplied was in the chloride form, was converted to the hydroxide form with 1 M aqueous NaOH as shown in reaction (3).



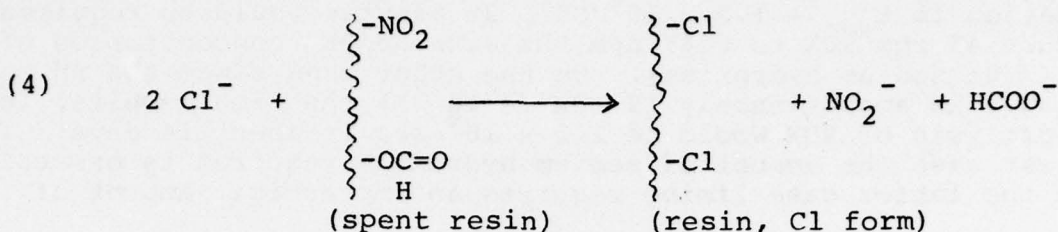
⁵ (a) $-d(\text{RDX})/dt = k_2(\text{OH}^-)(\text{RDX}) = k_1(\text{RDX})$

(b) $k_1 = k_2(\text{OH}^-) = 1/t_{\text{sec}} \times \ln(\text{RDX}_0/\text{RDX}_t)$

(c) at 99% hydrolysis, $k_1 = 1/t_{\text{sec}} \times \ln 100$; $t_{\text{sec}} = \ln 100/k_2(\text{OH}^-) = 1.2 \times 10^4 / \text{OH}^-$ where $k_2 = 3.9 \times 10^{-3} \text{ l-mole}^{-1}\text{sec}^{-1}$.

⁶Amberlite 400 resin (Rohm & Haas Co., Philadelphia, PA); a styrene/divinyl benzene copolymer with trimethylammonium hydroxide groups; and Amberlite 410, same as 400 except polymer contains dimethylethanolammonium hydroxide groups.

Regeneration of the spent resin from reaction (2) was accomplished in two steps: (a) conversion of the spent resin to the chloride form with 1 M aqueous NaCl shown in reaction (4), and



(b) conversion of the chloride form of the resin to the hydroxide form as already outlined in reaction (3).

The maximum moles of OH^- obtainable by reaction (3) from the Cl form of the resin was found to be 1.75×10^{-3} moles OH^- /gram resin (equivalent to 1.22 moles/liter and 34.7 moles/cubic ft).

The homogeneous aqueous hydrolysis of RDX in basic solution and the hydrolysis of RDX on basic resins appear to proceed by a similar mechanism. Consumption of hydroxide ion and the production of nitrite ion are essentially the same for both processes, Table 1. Since $\text{OH}^-_{\text{consumed}}/\text{RDX}_{\text{reacted}} = 3.0$, equation (5) may be written for the theoretical number of resin volumes, RV_{max} , that may be treated,

$$(5) \quad \text{RV}_{\text{max}} = \frac{\text{RL}_{\text{OH}}}{3 \text{ M}}$$

where RL_{OH} is the resin hydroxide loading factor expressed in moles OH^- /liter of resin and M is the molar concentration of the RDX solution. At the maximum hydroxide loading of resin ($\text{RL}_{\text{OH}} = 1.22$ moles OH^- /liter of resin) used to treat a saturated aqueous solution of RDX ($\text{M} = 2.03 \times 10^{-4}$ moles RDX/liter), $\text{RV}_{\text{max}} = 2.01 \times 10^3$ resin volumes. This maximum resin volume value assumes, of course, that depletion of the OH^- from the resin is caused by RDX alone.

According to equation (5), RV_{max} is proportional to the hydroxide loading factor, RL_{OH} . That this is approximately true is shown by the data in Table 2. A concentration of 1.98×10^{-4} M RDX (44 ppm) was metered through both resins separately and the effluent monitored for RDX by benzene extraction and vapor phase chromatographic analysis with the Ni-63 electron capture detector⁷. Since the absolute amounts of resin in both cases were quite different, 5.12 and 10.00 grams, respectively, the total amount of solution treated at a particular point was normalized by expressing the volume in terms of resin volumes.

⁷J. C. Hoffsommer, J. Chromatog., 51, 243-251 (1970).

TABLE 1

MOLE RATIOS, HYDROXIDE ION REACTED/RDX HYDROLYZED, AND NITRITE ION FORMED/RDX HYDROLYZED FOR THE BASIC HYDROLYSIS OF RDX IN WATER AND ON ION-EXCHANGE RESINS

Hydrolysis Conditions	Mole Ratio	
	OH ⁻ /RDX	NO ₂ ⁻ /RDX
heterogeneous ^a	3.0 ± 0.05 (3) ^b	1.26 (3) ^c
homogeneous ^d	-	1.19 ± 0.07 (9)
ion-exchange resin ^e	3.0 ± 0.1 (2)	1.2 ± 0.1 (2) ^f

a. 0.024 to 0.047 g RDX hydrolyzed in excess standard 0.1 N NaOH; excess base determined by back titration with standard 0.1 N HCl.

b. Numbers in parentheses indicate number of determinations.

c. NO₂⁻ determined by Griess method: P. Griess, Ber. Deut. Chem. Ges., 12, 426; given in F. D. Snell, "Colorimetric Methods of Analysis," Vol 2, Van Nostrand, New York, N.Y., 3rd ed., 802-804 (1949).

d. 7.0×10^{-6} to 2.0×10^{-4} M RDX hydrolyzed in 2.0×10^{-2} to 9.5 M aqueous NaOH.

e. Amberlite 400 and 410 resin; OH⁻ completely consumed by RDX; extent of RDX reaction estimated graphically from a plot of resin volumes vs RDX concentration in effluent.

f. NO₂⁻ displaced by 1 M NaCl and determined by Griess method of analysis.

TABLE 2

HYDROLYSIS OF RDX ON STRONGLY BASIC ION-EXCHANGE RESINS. VARIATION OF RESIN VOLUMES (RV) TREATED AS A FUNCTION OF RESIN HYDROXIDE LOADING, RL_{OH}

Resin # 1, $RL_{OH} = 0.278^a$			Resin # 2, $RL_{OH} = 1.22^d$		
RV_1	% RV_{1max}^b	Effluent RDX ^c ppm	RV_2	% RV_{2max}^e	Effluent RDX ^f ppm
35	7.5	<0.04	308	15.0	<0.01
78	16.7	<0.04	420	20.4	<0.01
100	21.4	<0.04	539	26.2	<0.01
165	35.3	0.08	693	33.7	0.026
219	46.8	0.25	766	37.2	0.048
262	56.0	0.52	805	39.2	0.11
289	61.8	0.89	1064	51.8	0.27
358	76.5	2.49	1113	54.2	0.67
386	82.5	2.88	1239	60.3	1.72
408	87.2	6.03	1281	62.4	3.3

a. Units, moles OH^- /liter; 5.12 g (7.31 ml) Amberlite 400 with 2.04×10^{-3} moles OH^- loading.

b. $RV_{1max} = 468$ resin volumes.

c. Flow rate, 0.28 RV/min; RDX feed, 1.98×10^{-4} M (44 ppm).

d. Units, moles OH^- /liter; 10.00 g (14.3 ml) Amberlite 410 with 1.75×10^{-2} moles OH^- loading.

e. $RV_{2max} = 2,054$.

f. Flow rate, 0.08 RV/min; RDX feed, 1.98×10^{-4} M (44 ppm).

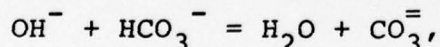
Comparing RV_1 and RV_2 at similar RDX effluent concentrations e.g., 0.25 and 0.27 ppm, respectively, it can be calculated that $RV_2/RV_1 = 4.8$, while the corresponding $(RL_{OH})_2/(RL_{OH})_1 = 4.4$.

Comparing both resins at an RDX effluent concentration of 0.5 ppm we find 56% RV_{max} for resin #1 and 53% RV_{max} for resin #2. In other words, at a point where 55 ± 2% of the available OH^- groups have been reacted or displaced, we may expect an RDX effluent concentration of approximately 0.5 ppm.

Figure 1 shows the relationship between the number of resin volumes of 44 ppm aqueous RDX passed through an amberlite 400 basic ion-exchange resin and the effluent concentration of RDX. Starting at about 320 resin volumes (1 ppm RDX), a rapid increase of the RDX effluent concentration occurs until at about 3 ppm RDX the curve becomes quite steep with a linear slope. From 165 resin volumes (35% RV_{max}) to 320 resin volumes, there is a linear increase in RDX effluent concentration from 0.08 to 1.0 ppm.

Since in most cases RDX will be found in tap water and tap water contains varying amounts of anions (notably, HCO_3^- , SO_4^{2-} , and Cl^-), it seemed worthwhile to study the displacement of hydroxide ion from the basic ion-exchange resin by tap water alone. The extent of this displacement is shown in Table 3. The hydroxide displacement is fairly constant at $1.8 \pm 0.2 \times 10^{-5}$ moles OH^-/RV of tap water effluent at a concentration of $2.5 \pm 0.3 \times 10^{-3}$ M OH^- until 225 resin volumes have been passed through the resin and approximately 50% of the total available hydroxide ions have been displaced. Afterwards there is a marked decrease in OH^- displacement.

After 53.6% of the total OH^- had been displaced, Table 3, it was determined by displacement with 1 M NaCl that 21.2% of the total OH^- remained on the resin⁸. The remaining 25.2% of the hydroxide is considered to be consumed in chemical reactions, i.e., neutralization and precipitation. The molar concentration of HCO_3^- in tap water was determined to be 1.13×10^{-3} M (69 ppm) by acid titration with methyl orange indicator. At this concentration, 1.82×10^{-3} moles of OH^- (22.8% of total) would be expected to be consumed in the neutralization reaction:



after the passage of 225 resin volumes of tap water and assuming complete reaction.

⁸Since the anion content of the tap water remains constant during a cycle, it is not surprising that the concentration of displaced OH^- ions decreases as the resin sites become occupied with tap water anions.

TABLE 3

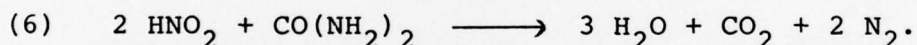
DISPLACEMENT OF HYDROXIDE ION FROM BASIC ION-EXCHANGE RESIN BY ANIONS^a IN TAP WATER

Resin Volumes, RV ^b	Total Moles ^c OH ⁻ Displaced	Moles OH ⁻ Displaced ^d Resin Volume	%Total ^e OH ⁻ displaced
34.6	62 X 10 ⁻⁵	18 X 10 ⁻⁶	7.8
76.9	146 X 10 ⁻⁵	20 X 10 ⁻⁶	18.3
144	272 X 10 ⁻⁵	19 X 10 ⁻⁶	34.0
225	396 X 10 ⁻⁵	16 X 10 ⁻⁶	49.5
305	424 X 10 ⁻⁵	35 X 10 ⁻⁷	53.0
371	429 X 10 ⁻⁵	8 X 10 ⁻⁷	53.6 ^f

- a. Approximate anion content of area water (major components):
 HCO_3^- , 20 to 200 ppm; SO_4^{2-} , 5 to 70 ppm; Cl^- , 5 to 40 ppm;
 SiO_3^{2-} ~5 ppm (Data from Dalecarlia Filtration Plant, Wash., D.C.).
- b. 5.00 g (7.14 ml) Amberlite 410 basic resin.
- c. Determined by titration with standard 0.1 N HCl.
- d. Incremental values.
- e. 5.00 g (7.14 ml) Amberlite 410 resin; total OH⁻, 8×10^{-3} moles.
- f. An additional 1.7×10^{-3} moles (21.2%) was obtained by displacement with 1 M NaCl.

Tap water also contains appreciable amounts of the cations, Ca^{+2} , and Mg^{+2} in amounts of 40 to 60 ppm and 0.2 to 10 ppm, respectively (data from Dalecarlia Filtration Plant, Wash., D.C.). After 4 to 5 cycles, a white precipitate was observed to build up near the top of the resin (downward flow) and essentially stopped the free flow through the resin. Presumably the OH^- and CO_3^{+2} ions produced by anionic displacement react with the Ca^{+2} and Mg^{+2} to form insoluble hydroxides and carbonates. Considering the K_{sp} values of these products, it is most likely that this precipitate is a mixture of $\text{Mg}(\text{OH})_2$ (K_{sp} , 1.2×10^{-11} at 18°C) and CaCO_3 (k_{sp} , 8.7×10^{-9} at 15°C). Treatment of the resin with 1 M HCl dissolved this precipitate immediately (gassing) and restored the original free flow of the resin (somewhat over 2 resin volumes/min).

In Tables 4 and 5 are presented the results for the resin breakthrough/regeneration parameters for the hydrolyses of RDX in tap water on basic Amberlite 410 ion-exchange resins for laboratory and pilot-scales, respectively. For each cycle, points near the breakthrough point (0.3 to 0.5 ppm RDX) are included. Regeneration of the resin on a laboratory scale was accomplished by the passage of 2 resin volumes of 1 M HCl through the resin, followed by water rinsing, then 2 resin volumes of 1 M NaOH. Regeneration of the resin on a pilot-scale was accomplished by some modifications of this procedure. Resin regeneration was carried out downflow on a laboratory scale (1.43×10^1 ml/resin volume), but upflow on a pilot scale (4.5×10^3 ml/resin volume). In the HCl step for the pilot scale regeneration cycles 2,3,4,5,6, and 7, urea was used to avoid the formation of nitrous acid by the reaction⁹ shown in equation (6).



In general, an effluent content of ~ 0.5 ppm RDX was found at approximately 280 resin volumes ($13\% \text{RV}_{\text{max}}$) on a laboratory scale and approximately 180 resin volumes ($8.4\% \text{RV}_{\text{max}}$) on a pilot scale for eight cycles in each case. The somewhat lower efficiency of the scale-up may be partially rationalized on the basis of a different RL_{OH} for the large scale hydrolysis. RL_{OH} for the scale-up was assumed to be the same as that determined for the small scale hydrolyses, namely, 1.22 moles OH^- /liter of resin¹⁰. Furthermore,

⁹I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The MacMillan Co., 3rd ed., p 599 (1952).

¹⁰Due to the handling of large volumes of 1 M NaCl that would be necessary to displace the total OH^- ion from the basic resin on a pilot scale, RL_{OH} was not determined.

variable anion content of the tap water would alter the hydroxide ion displacement from the basic resin and would change the rate of resin depletion, Table 3.

The basic ion-exchange resin appears to be completely regenerable for both the laboratory and pilot-scale RDX hydrolyses, Tables 4 and 5. Since approximately 50% of the OH^- will have been displaced at 225 resin volumes, Table 3, and at ~50% resin depletion RDX appears in the effluent at ~0.5 ppm, Table 2, it is not surprising that the resin breakthrough occurs at 180 and 280 resin volumes for the large and small scale RDX hydrolyses, respectively. Comparing the results obtained in Table 2 for resin #2 and Table 4, it is apparent that the anionic content of the tap water reduces the efficiency of the resin by 74% from 1,088 to 280 resin volumes.

III. EXPERIMENTAL SECTION

RDX/Resin Hydrolysis, Laboratory Scale

The resin columns were prepared by placing 5 and 10 grams of resin into 1.0 and 3.5 cm diameter glass chromatographic tubes, respectively. A small quantity of glass wool was used to support the resin while the bottom of the tubes were fitted with take-off stems and stopcocks. RDX solutions were prepared by either (a) stirring solid RDX in tap or distilled water for 6 to 8 hours and filtering through 0.4 micron millipore filters, or (b) metering (Cole Palmer, Masterflex, Model 7565) tap or distilled water through a 3.5 cm diameter glass chromatographic column containing 4 to 5 grams of solid RDX supported by a glass wool plug. In practice, it was found convenient to attach the glass column containing the solid RDX directly to the resin column, Figure 2. The RDX concentration was monitored by taking samples from the take-off tube at the head of the resin column.

The total volume of effluent from the resin column was collected and its volume determined. At the same time a small effluent sample was taken directly from the resin column for analysis. Regeneration of the spent resin was accomplished as follows: (a) downflowing 4 resin volumes of 1 M aqueous HCl through the resin at a rate of 0.1 to 0.2 resin volumes/min., (b) rinsing the resin with water until the effluent pH was between 6 and 7, (c) downflowing 4 resin volumes of 1 M aqueous NaOH through the resin at a rate of 0.1 to 0.2 resin volumes/min., and (d) rinsing the resin with water until the effluent pH was between 7 and 8.

Resin Effluent Analysis

Five millimeter (5.0 ml) aqueous effluent samples from the resin were extracted with 5.0 ml of benzene which was then analyzed with a Hewlett-Packard Model 5750 research gas chromatograph⁷. In general, chromatographic conditions were

TABLE 4

RESIN BREAKTHROUGH/REGENERATION PARAMETERS FOR RDX SOLUTION IN TAP WATER, LABORATORY SCALE

Cycle ^a	Effluent Resin Volumes ^b	RDX in Effluent, ppm ^c	Percentage Theoretical Resin Volumes ^d
1	26.5	<0.01	1.3
1	142	<0.01	6.8
1	178	0.090	8.5
1	197	0.33	9.4
1	207	0.48	9.9

2	110	<0.01	5.2
2	246	<0.01	11.7
2	342	0.65	16.3

3	143	<0.01	6.8
3	391	0.29	18.7

4	124	<0.01	5.9
4	265	0.013	12.6
4	304	0.042	14.5
4	401	3.4	19.1

5	157	<0.01	7.5
5	204	<0.01	9.7
5	288	0.023	13.7
5	332	0.29	15.8

6	195	0.064	9.3
6	287	0.59	13.7

7 ^e	154	<0.01	7.3
7	299	0.016	14.3
7	382	0.22	18.2

8	172	<0.01	8.2
8	306	<0.01	14.6
8	332	<0.01	15.8
8	353	1.19	16.8

a. Column regeneration between cycles: 2 resin volumes, RV, 1 M HCl; 2 RV 1 M NaOH.

b. 10.00 g (14.3 ml) Amberlite 410 resin containing 0.0175 moles OH⁻ ion (equivalent to 1.22 moles OH⁻/liter of resin).

c. RDX feed, 1.6×10^{-4} to 2.2×10^{-4} M (36 to 50 ppm); flow rate, 0.1 RV/min.

d. $RV_{max} = 2,140 \pm 300$ resin volumes.

e. Column regeneration, 1 RV 1 M HCl; 2 RV 1 M NaOH.

TABLE 5

RESIN BREAKTHROUGH/REGENERATION PARAMETERS FOR RDX SOLUTION IN TAP WATER, PILOT SCALE

Cycle	Resin Volumes ^a of Effluent	RDX ^b in Effluent, ppm	Percentage Theoretical ^c Resin Volumes
1 ^d	137	0.07	6.4
1	162	0.17	7.6
1	200	0.66	9.3
2 ^e	192	0.20	9.0
2	207	0.69	9.7
2	214	1.6	10
3 ^e	34	0.01	1.6
3	166	1.2	7.8
4 ^f	138	0.03	6.4
4	172	1.6	8.0
5 ^g	169	0.062	7.9
5	177	0.36	8.3
5	181	1.1	8.5
6 ^h	139	0.11	6.5
6	144	0.40	6.7
6	150	1.9	7.0
7 ⁱ	161	0.047	7.5
7	169	0.58	7.9
7	174	3.2	8.1
8 ^j	173	0.17	8.1
8	183	0.44	8.6
8	189	1.6	8.8

- a. 1 resin volume, RV, = 1.6 cubic ft (45 liters) Amberlite 410; calculated resin hydroxide loading, RL_{OH} , = 1.22 moles OH/liter resin (34.3 moles OH/cu. ft).
- b. Cycle, (Average ppm RDX feed): 1, (30); 2, (39); 3, (46); 4, (46); 5, (44); 6, (41); 7, (44); 8, (47).
- c. RV_{max} = 2,140 \pm 300 resin volumes.
- d. through j.: Individual resin regeneration procedures; upflow; steps separated by semicolon. d. 4 RV 1 M NaOH. e. 0.77 RV (0.05 M urea, 0.86 M HCl, 0.56 M NaCl); 2.6 RV 0.92 M NaCl; 5.3 RV 0.75 M NaOH. f. 1 RV (0.04 M urea, 1.3 M HCl); 0.8 RV 1.6 M HCl; 5.3 RV 0.75 M NaOH. g. 1.1 RV (0.035 M urea, 2 M HCl); 4 RV 0.75 M NaOH. h. 1.1 RV (0.035 M urea, 2 M HCl); 2.7 RV 0.75 M NaOH. i. 1.1 RV (0.035 M urea, 2 M HCl); 2.7 RV 0.98 M NaCl; 2.7 RV 0.94 M NaOH. j. 4 RV 1 M NaCl; 1.8 RV 0.29 M HCl; 4 RV 1 M NaOH.

as follows: 4 ft X 1/4 in. glass column packed with 2.95% Dexsil 300 GC on Chromosorb WAWDMCS 80/100 mesh; column temperature, 175°C; injection port, 180°C; carrier gas, argon/methane, 95/5; flow rate 192 ml/min.; Ni-63 electron capture detector temperature, 290°C; pulse, 150 microseconds; attenuation, X80. TNT was used as internal standard. Dilutions were made so that the final concentrations were approximately 7.4×10^{-6} M RDX and 7.1×10^{-7} M TNT, and retention times were approximately 200 and 80 seconds, respectively. Peak heights were used to calculate RDX concentrations by comparison to standards of known concentrations.

RDX/Resin Hydrolysis, Pilot Scale

The schematic for the large scale setup for the hydrolysis of RDX with basic resins is shown in Figure 3. Diagrams for the individual resin column and RDX columns are shown in Figures 4 and 5, respectively. Tap water was prefiltered through 100 micron filters and then through 10 micron filters. The RDX columns were pyrex glass with an individual volume of approximately 300 ml and were loaded with a total of approximately 2.5 lbs of solid RDX. A flowmeter in series indicated rate of addition of the RDX aqueous feed while a total volume meter allowed accurate measurement of the total volume processed. Flow rates were between 0.067 and 0.17 resin volumes/minute (0.79 and 2.0 gallons/minute). A sampling outlet, in line, was used to determine the RDX concentration in the feed solution. Samples of the feed solution were taken at the same time that the resin effluent samples were obtained at approximately 4-hour intervals and at 1-hour intervals when the effluent concentration reached 0.05 to 0.1 ppm RDX.

The column containing the basic resin was designed for upflow regeneration by means of an electric pump equipped with an electrical controller. Regeneration of the spent resin was accomplished as follows: (a) upflowing 1 to 4 resin volumes of aqueous solutions containing NaCl, urea and HCl through the resin, (b) rinsing the resin with water until the effluent pH was between 5 and 6, and (c) upflowing 2.7 to 5.3 resin volumes of approximately 1 M aqueous NaOH through the resin. Flow rates during regeneration were maintained between 0.05 and 0.1 resin volumes/minute for each step. The individual amounts of materials and concentrations used for each cycle are given in the footnotes of Table 5. Urea and HCl were included to destroy the nitrous acid and the insoluble basic precipitates as previously outlined in the Results and Discussion Section. In the interest of economy and efficiency the regeneration procedures for cycles 2 and 8 are to be preferred. Effluent from the resin was analyzed for RDX content as previously described.

IV. SUMMARY AND CONCLUSIONS

The strongly basic ion-exchange resins, Amberlite 400, and Amberlite 410 have been found to be extremely effective in removing and degrading small amounts of RDX contained in large volumes of water as this water is passed through the resin. Both laboratory and pilot scale studies show no resin degradation after 8 regeneration cycles. One cubic foot of resin has been found capable of removing and degrading 99% of the RDX in 1,300 gallons of tap water containing 45 ppm RDX so that the effluent RDX is less than 0.5 ppm. In contrast, laboratory studies show that one cubic foot of resin could treat 8,200 gallons of 45 ppm RDX in de-ionized water. In conclusion, strongly basic ion-exchange resins offer a good method for the removal of RDX from large volumes of water provided the anion and/or acid content of water is not large.

It is recommended that the use of strongly basic ion-exchange resins to remove and degrade other base sensitive explosives from water be investigated. Initial studies show that HMX is degraded on the basic resin and there is no reason to believe that other compounds such as nitrate esters might not be similarly degraded.

V. ACKNOWLEDGEMENT

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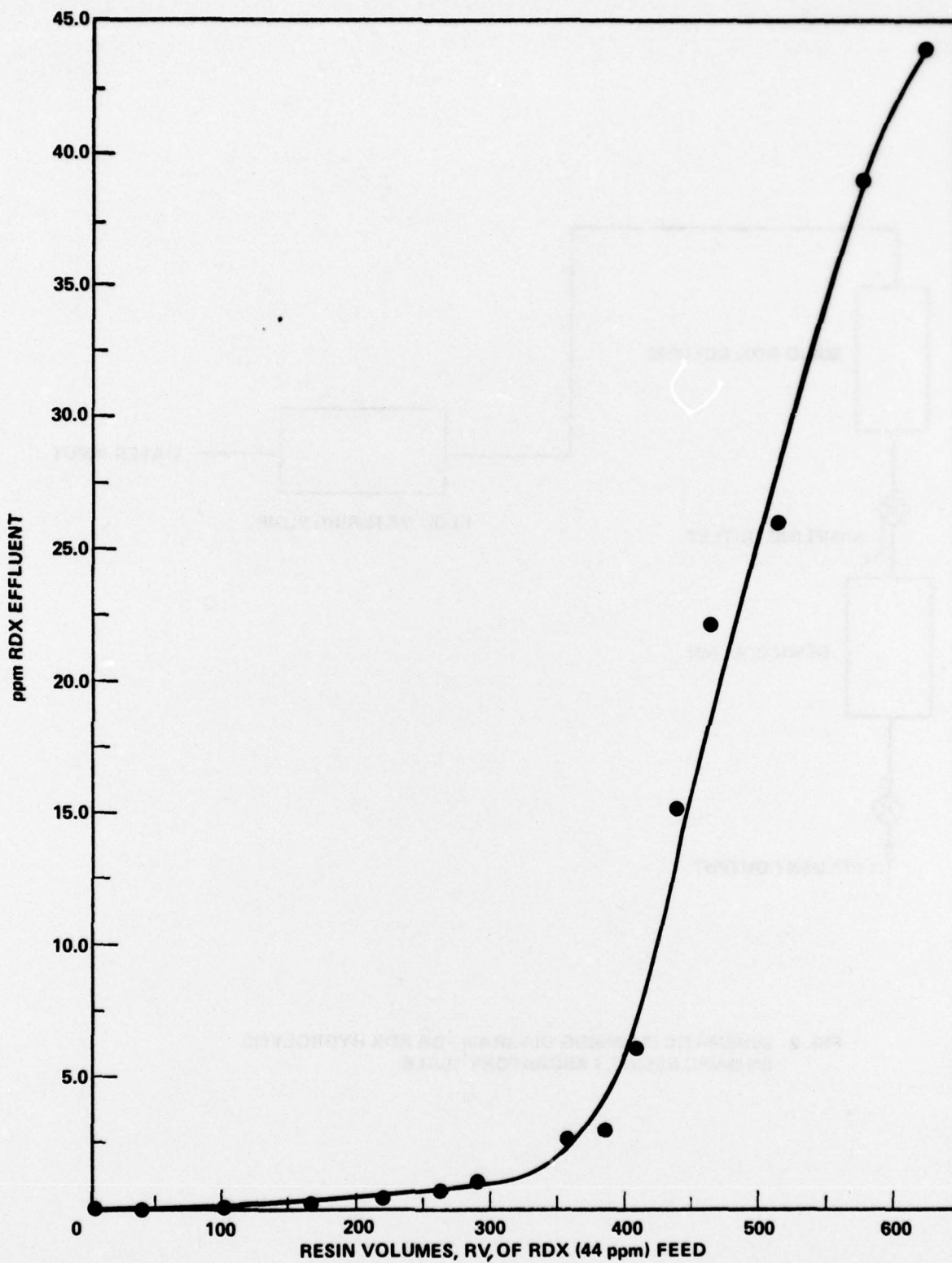
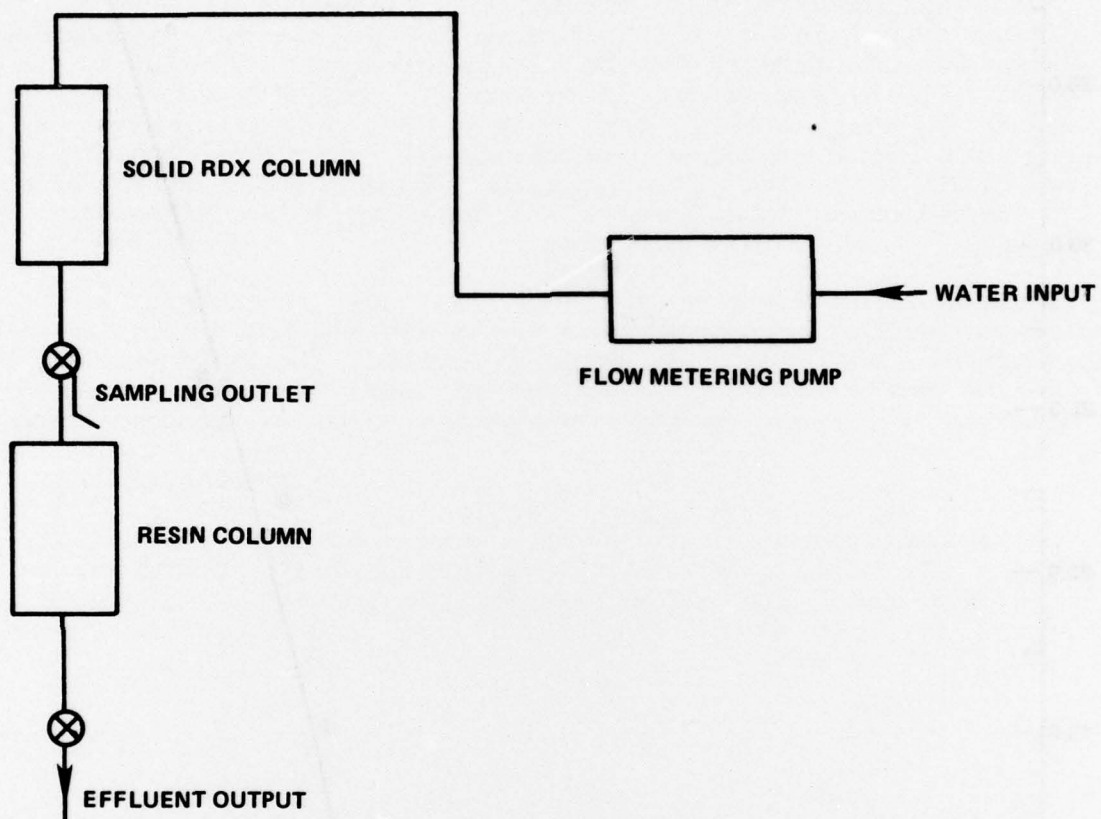


FIG. 1 HYDROLYSIS OF AQUEOUS RDX ON AMBERLITE 400 BASIC ION-EXCHANGE RESIN (RESIN HYDROXIDE LOADING, $RL_{OH} = 0.278$ MOLES OH/LITER)



**FIG. 2 SCHEMATIC PLUMBING DIAGRAM FOR RDX HYDROLYSIS
ON BASIC RESINS, LABORATORY SCALE**

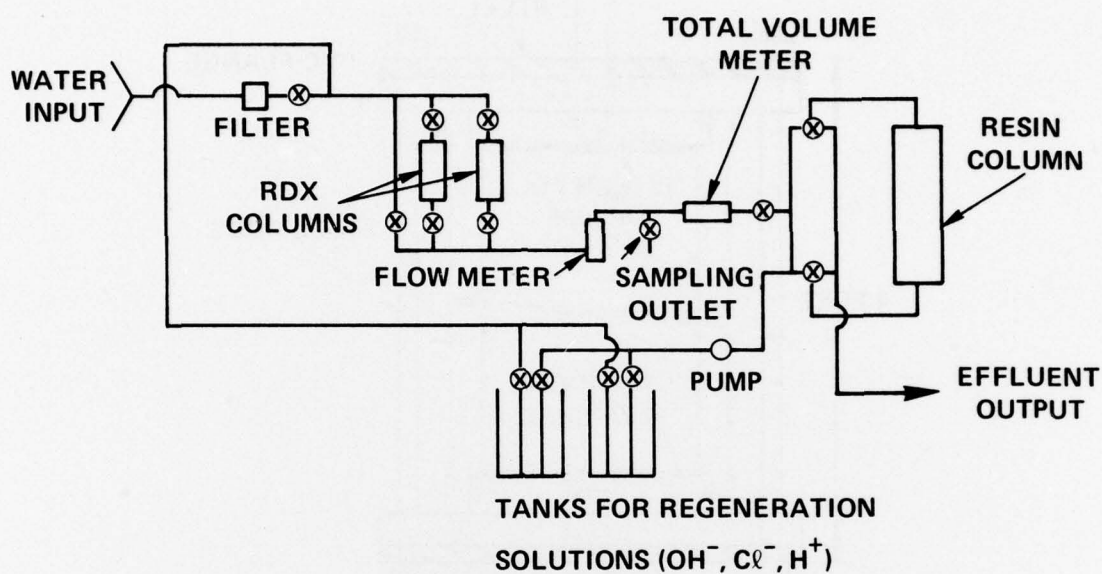


FIG. 3 SCHEMATIC PLUMBING DIAGRAM FOR RDX HYDROLYSIS ON BASIC RESINS, PILOT SCALE

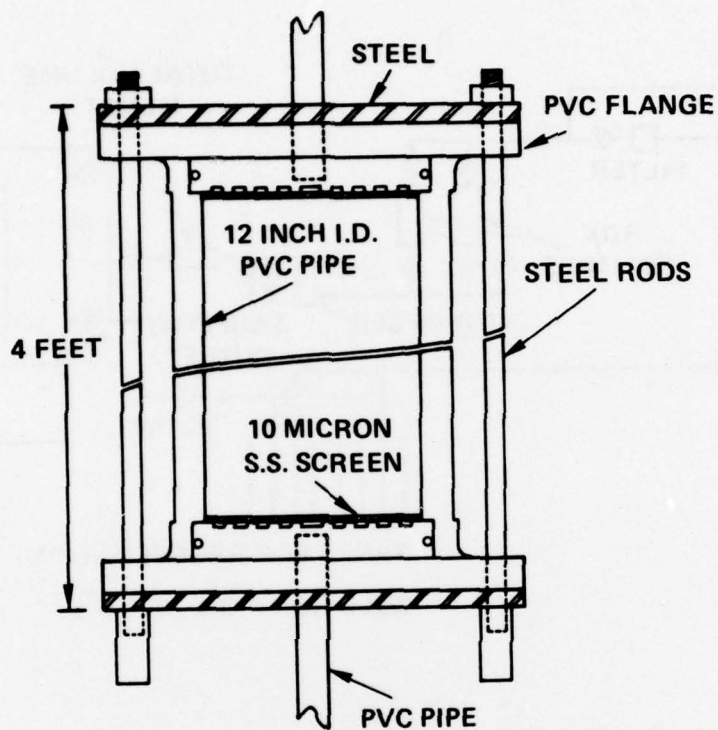


FIG. 4 COLUMN FOR CONTAINING BASIC ION-EXCHANGE RESIN

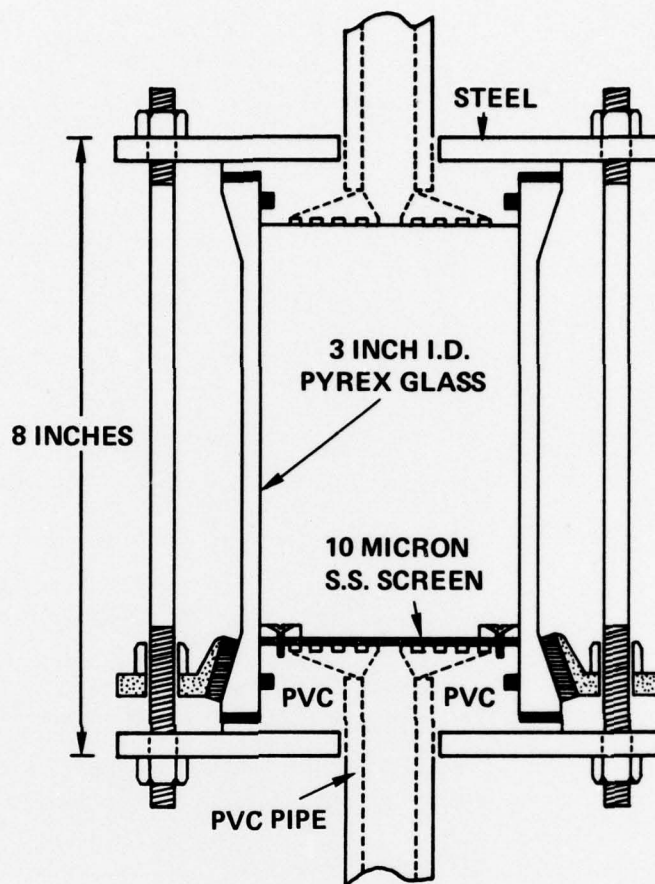


FIG. 5 RDX COLUMN FOR GENERATING RDX CONTAMINATED WATER

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